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PAPER

# Syntheses, crystal structures, photophysical and theoretical studies of 1,3,2-benzodiazaborolyl-functionalized diphenylacetylenes†

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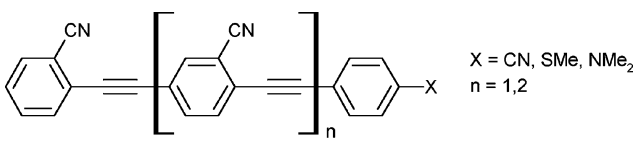
A series of diphenylacetylenes with one 1,3,2-benzodiazaborolyl end group (BDB) and a second end group X (X = H, OMe, $NMe_2$, SMe, CN and BDB) were synthesized using established 1,3,2-benzodiazaborole methodologies. The 1,3,2-benzodiazaborolyldiphenylacetylenes with X = *p*-H (**4**), *p*-OMe (**5**), *p*-$NMe_2$ (**6**), *p*-SMe (**7**) and *p*-CN (**8**) end groups are functionalized with cyano groups at the central ring in an *ortho*-position to the triple bond. Molecular structures of **2**, **3**, **5**, **6** and **7** were determined by X-ray diffraction. These borylated systems show intense blue luminescence in cyclohexane, toluene, chloroform, dichloromethane and tetrahydrofuran, whereas green luminescence was observed in acetonitrile solutions. Thereby Stokes shifts in the range 1700–8600 $cm^{-1}$ and quantum yields of 0.60–1.00 were observed in cyclohexane solutions. The absorption maxima (308–380 nm) are well reproduced by TD–DFT computations (B3LYP/G-311G(d,p)) and arise from strong HOMO–LUMO transitions. The LUMOs in all the molecules under study are mainly located on the diphenylacetylene bridge, while with the exception of the dimethylamino derivative **6**, the HOMO is largely benzodiazaborolyl in character. Thus, the S1←S0 absorption bands are assigned to π(diazaborolyl)–π*(diphenylacetylene) transitions. In contrast to this, in compound **6** the HOMO is mainly represented by the terminal dimethylaminophenyl unit. While calculated ground state dipole moments $\mu_g$ are small (1.1–7.5 D), experimentally determined changes of the dipole moments upon excitation are large (14.8–19.7 D) and reflect a significant charge transfer upon excitation. NLO activities of the rod-structured compounds **2**, **4**, **6** and **8** are indicated by calculated static first-order hyperpolarizabilities $\beta$ up to $76.8 \times 10^{-30}$ esu.

## Introduction

Molecular and polymeric compounds based on the phenylene–ethynylene motif have been the subject of considerable interest in recent years. Linear and cruciform structured phenylene–ethynylenes with electron donating and accepting substituents have been intensively investigated for their potential application as efficient light emitters in electro–optical devices, as semiconductors, as well as materials with second- and third-order non-linear properties.[1–3] Fundamental knowledge of the structure–efficiency relationship is required to create compounds with defined properties.[4] This could principally be achieved by the variation of the length of the conjugated π-system as well as by the introduction of donor and/or acceptor functionalities at appropriate positions of the molecules. It has been recognized that larger net dipoles and linear electron conducting pathways provide the largest bathochromic shifts.[4] Yamaguchi *et al.* have demonstrated that oligophenylene–ethynylenes **I** with donor end groups and cyano substituents flanking the rod shaped scaffold are beneficial for the wavelength of the emission and the quantum efficiencies of these species.[5,6] Interestingly, the dipole moments in the ground- and excited states of **I** did not differ significantly.




**I**

Boron-containing functionalities in phenylene–ethynylenes type compounds are scarce.[7,8] Only recently Marder *et al.* reported on the syntheses and photophysics of dimesitylboryl substituted 4-(arylethynylene)anilines of type **II**.[9]

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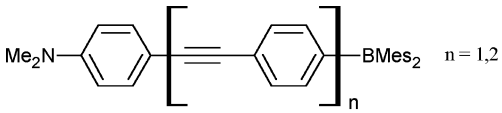
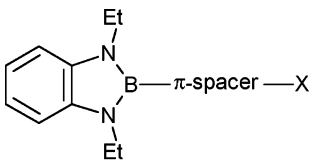
† Electronic supplementary information (ESI) available: Tables of atomic coordinates for [B3LYP/6-311G(d,p)] optimized geometries, values of total energies and ionization energies (IEs) of **2–9**. CCDC reference numbers 780599–780603. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01410a




**II**

One of our current research interests is focused on the chemistry of 1,3,2-diazaboroles.[10,11] Thereby, we carried out studies on the syntheses and optical properties of extended π-conjugated systems with 1,3,2-diazaborolyl- and 1,3,2-benzodiazaborolyl-substituents, which gave intense blue luminescence when irradiated with UV-light.[12–14] Thereby it became evident that the 10 π-electron diazaborole (BDB) fragment functions as a π-donor despite the presence of a three-coordinate boron contact atom. The donor strength of the BDB substituent has not been quantified as yet. Here we attempt to estimate the donor capacity of BDB experimentally by comparison with more common donors in line with Marder's method by evaluating first-order hyperpolarizabilities.[8] Thus, molecules of type **III**, where the diazaborolyl unit is separated from a substituent X by a π-conducting spacer, should be designed to study their photophysical properties, particularly dipole moments and first-order hyperpolarizabilities $\beta$.




**III**

With donors of similar strength as the BDB unit the dipole moments and $\beta$-values are expected to decrease markedly, and in case of an ideal match they should vanish completely. As the π-spacer we selected diphenylacetylene as it leads to rod-like molecules with a longer π-skeleton and red shifts in absorption and emission in comparison to the previously studied 2-phenylethynyl-1,3,2-benzodiazaboroles.[14] Moreover, the decreased sensitivity to moisture of the B–C-linkage in phenylboranes with respect to ethynylboranes should be advantageous for the use of the new materials in OLEDs.

With respect to Yamaguchi's work[5,6] the incorporation of cyano side groups into the molecules is envisaged. In doing so, LUMO energies are lowered and electron transport by these species in OLEDs should be facilitated as well.

## Results and discussion

A prerequisite for the estimation of the influence of the cyano group on our systems is the availability of phenylacetylenes with one or two benzodiazaboryl substituents as a reference.

The protocol for the synthesis of 2-[4′-phenylethynyl]phenyl-1,3-diethyl-1,3,2-benzodiazaborole (**2**) involved the lithiation of 4-bromodiphenylacetylene[15] by *n*-butyllithium and coupling of the obtained lithium aryl with 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (**1**).[16] Crystallization of the solid reaction residue from an *n*-pentane–dichloromethane mixture afforded colorless needles of product **2** in 37% yield (Scheme 1).

4,4′-Dibromo-diphenylacetylene was synthesized by the Sonogashira coupling of trimethylsilylacetylene with 2 equiv. of *para*-bromoiodobenzene.[15] Lithiation of this intermediate by two molar equiv. of *n*-butyllithium and the subsequent addition of two equiv. of **1** to the reaction mixture led to product **3** as colorless needles after crystallization from methylcyclohexane–$CH_2Cl_2$ (yield 48%) (Scheme 2).

The Sonogashira coupling of 2-bromo-5-iodobenzonitrile[17] with *p*-substituted arylacetylenes furnished 5-bromo-2-(arylethynyl)benzonitriles,[6] which were metallated in THF solution at −110 °C by *n*-butyllithium and then combined with 2-bromo-1,3,2,-benzodiazaborole (**1**). Colorless crystals of compounds **4–8** were obtained in 38–77% yield by extraction of the reaction residue with *n*-hexane and recrystallization of the crude products (Scheme 3).

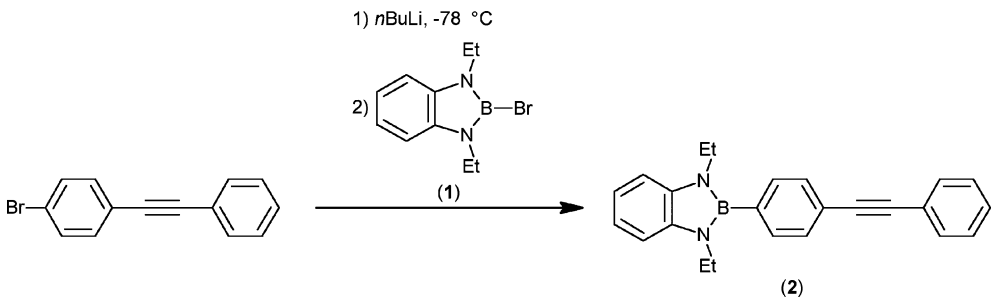
For the lithiation of the precursor with *n*-butyllithium and subsequent treatment of the transient aryllithium species with 2-bromo-1,3,2-benzodiazaborole (**1**) it was crucial to maintain the temperature within the reaction vessel below −100 °C. Thus, the *n*-butyllithium solution as well as the solution of **1** had to be added sufficiently slow to avoid local warming, which invariably led to side reactions at the cyano function.

All the compounds synthesized here can be stored under an argon atmosphere for several weeks without decomposition. The $^{11}B\{^1H\}$-NMR spectra for the diazaboroles **2–8** displayed singlets at 27.4–28.6 ppm in line with other 2-aryl-1,3,2-benzodiazaboroles which revealed singlets at $\delta$ = 28.6 to 29.3 ppm.[13]

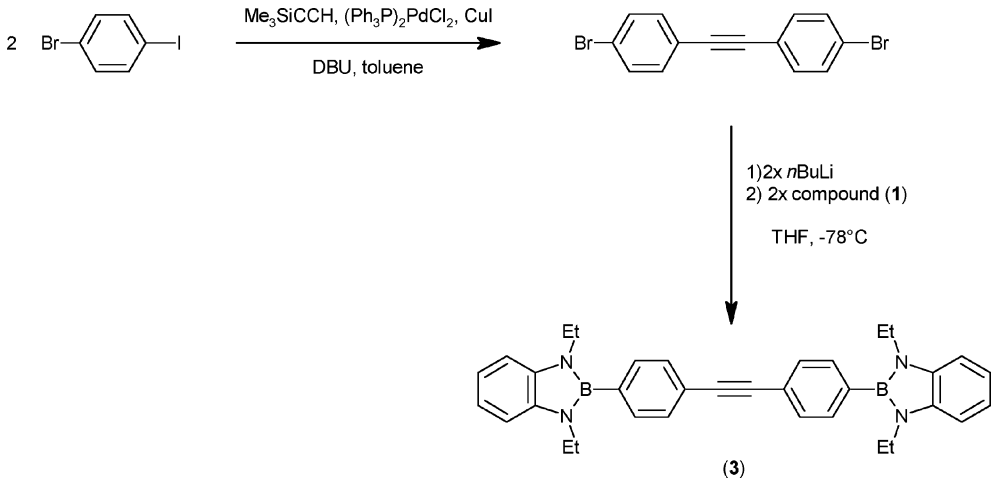
### X-Ray crystallography

Molecular structures were determined for five benzodiazaborolyl-functionalized diarylacetylenes **2**, **3**, **5–7** (Fig. 1, Table 7). Bond lengths and angles of interest are listed in Table 1.

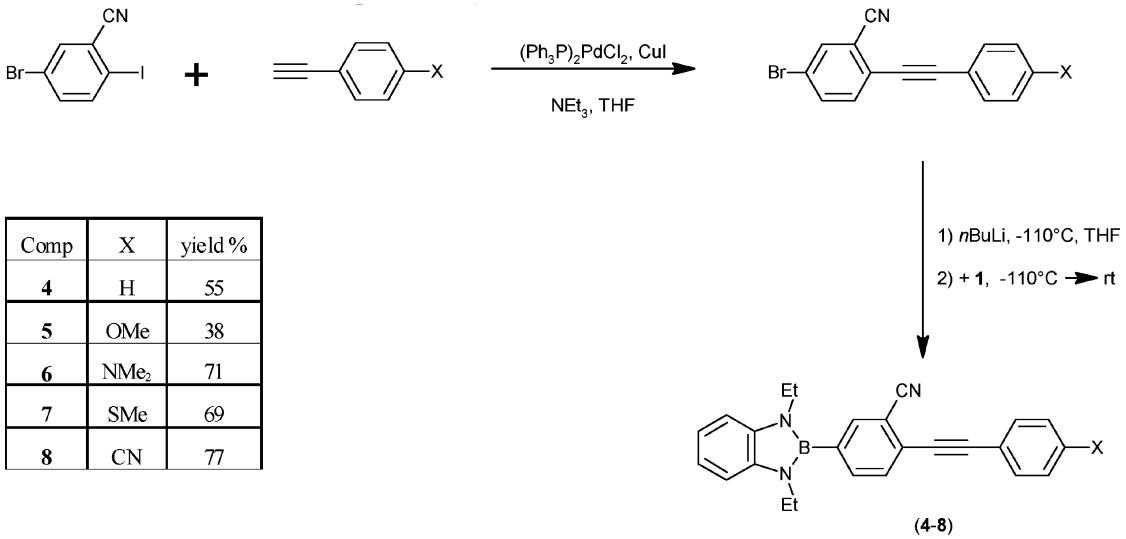
Molecule **3** lies on a crystallographic inversion center at the middle of bond C(17)–C(17A). For compound **2** the unit cell




**Scheme 1** Synthesis of compound **2**.




**Scheme 2** Synthesis of compound **3**.




| Comp | X | yield % |
|---|---|---|
| **4** | H | 55 |
| **5** | OMe | 38 |
| **6** | $NMe_2$ | 71 |
| **7** | SMe | 69 |
| **8** | CN | 77 |

**Scheme 3** Synthesis of compounds **4–8**.

contains two independent conformers, the bonding parameters of which are identical within 3 esd's.

The BN, CN and CC bond lengths within the 1,3-diethyl-1,3,2-benzodiazaborolyl groups [av. 1.43, 1.40, 1.41 Å] (see ESI†) in all the structures are virtually identical and coincide with those in numerous benzodiazaborole structures previously studied [12–14] The benzodiazaborole units are linked to the central arene moiety by single bonds B(1)–C(11) of 1.566 Å (av.). It is remarkable that in compounds **2**, **3** and **5** the *p*-phenylene rings contain two C–C bonds (C(12)–C(13) and C(15)–C(16)) which are slightly shorter than the remaining C–C contacts, indicating a small degree of quinoid character. In contrast to this in **6** and **7** no such behavior is evident. Both aryl rings are linked by a linear C–C triple bond of 1.20 Å (av.). The mutual orientations of the aromatic π-systems and their orientation with respect to the diazaborolyl groups are important, as better π-conjugation between the π-orbitals on boron and on the diphenylacetylene fragment would occur if the aromatic rings and the diazaborolyl groups are coplanar. The interplanar angles between the heterocycle and the adjacent arene ring range from 39.2 to 56.7° (av. 46.6°), where the extreme values are measured for the two independent conformers of **2**. In 1,4-bis- or 1,3,5-tris-*p*-benzodiazaborolylphenylbenzene values of 33.9–49.8° (average 46.2°) for the respective torsion angles were found previously.[13]

In the centrosymmetric molecule **3** the central diphenylacetylene part is planar, whereas in the two conformers of **2** both arene rings are tilted by 11.1° and 78.7°, respectively. In the remaining compounds the deviation from planarity increases on going from **5** (25.3°) *via* **7** (50.5°) to **6** (78.3°), which is in agreement with a very low rotational barrier about the carbon–carbon triple bond in all five compounds. A similar result was recently obtained for 2-[arylethynyl]-1,3-diethyl-1,3,2-benzodiazaboroles.[14b]

Thus, it is obvious that at least in the solid state no satisfactory π delocalization between the three ring units is present. It is worth mentioning that the distance N(4)–C(23) of 1.383(1) Å is consistent with multiple bonding, despite the fact that the amino group is slightly pyramidal (sum of angles 353.5°) and twisted by 24.4° out of the plane of the adjacent ring.

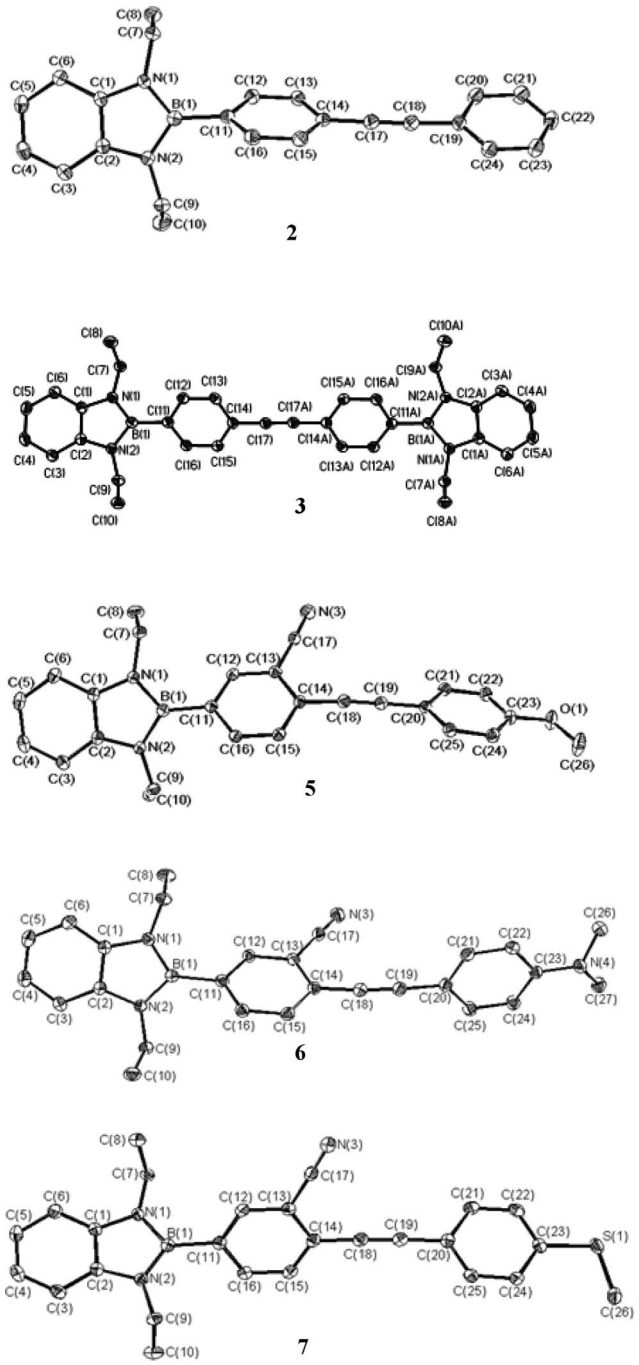



**Fig. 1** Molecular structures of **2**, **3**, **5**–**7**.

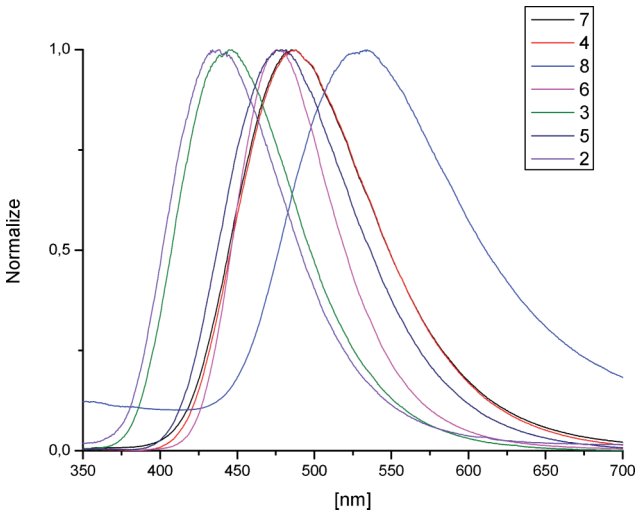



**Fig. 2** Emission maxima of **2**–**8** in $CH_2Cl_2$.

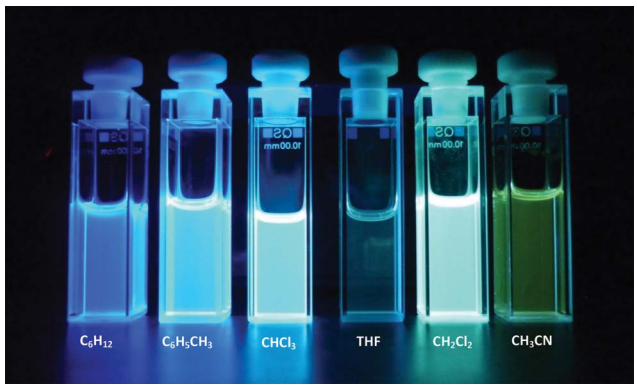



**Fig. 3** Photograph of the emission of **7** in different solvents.

### UV-visible and luminescence spectroscopy

The UV-Vis absorption and emission spectra of compounds **2**–**8** were determined in a variety of solvents (Fig. 2 and 3). Their absorption and emission maxima and their extinction coefficients are given in Table 2. In general all chromophores show intense absorption bands, which are not markedly influenced by the solvents (max. difference 10 nm). These small solvatochromic absorption shifts are consistent with small ground-state dipole moments. Interestingly, the insertion of a phenylene unit into the B–C (alkyne) bond of BDB–C≡C–Ph[14a] to afford **2** with an elongated π-system was accompanied by a slight blue shift of the UV-Vis absorption maximum $\lambda_{abs}$ (303 nm in **2** *vs.* 306 nm for BDB–C≡C–Ph in *c*-$C_6H_{12}$). A similar effect has been noted previously for donor/acceptor substituted phenylene–ethynylene oligomers and was attributed to statistically poorer donor/acceptor interactions in the ground state of the longer system due to an increased number of rotameric conformers of the more than two rings.[1j,9] The emission maximum of **2** (380 nm) is red shifted in comparison to the 2-phenylethynyl benzodiazaborole (361 nm), which is in agreement with the elongation of the π-system and an increased planarization of the molecule in the excited state. The extension of the rod-like structure of **2** by a second benzodiazaborolyl group to afford derivative **3** gives rise to a bathochromically shifted absorption maximum ($\lambda_{abs}$ = 314 nm). The emission maximum, however, (386 nm) is only slightly shifted. Upon incorporation of a cyano group at the central ring adjacent to the triple bond in **2** to give **4**, both, the absorption and emission maxima are red shifted by 21 and 27 nm respectively (in *c*-$C_6H_{12}$). In derivates **5** (X = OMe), **7** (X = SMe) and **6** (X = $NMe_2$) the donor end groups cause red shifts in the UV absorption of about 15, 25 and 56 nm in comparison to compound **4** (X = H) in *c*-$C_6H_{12}$. Remarkably, the emission maxima of **4** (407 nm), **5** (403 nm), **6** (403 nm) and **7** (408 nm) are not essentially influenced by the nature of the substituent in the *para*-position of the terminal aryl ring.

**Table 1** Selected bond lengths and angles for **2**, **3**, **5–7**

| | **2** | **3** | **5** | **6** | **7** |
|---|---|---|---|---|---|
| Bond lengths (Å) | | | | | |
| B–C | B(1)–C(11) 1.566(2) | B(1)–C(11) 1.564(2) | B(1)–C(11) 1.563(1) | 1.568(1) | 1.568(1) |
| B–N (av.) | B(1)–N(1) 1.431(1) | B(1)–N(1) 1.432(2) | B(1)–N(1) 1.438(1) | 1.434(1) | 1.434(2) |
| | B(1)–N(2) 1.432(2) | B(1)–N(2) 1.438(2) | B(1)–N(2) 1.437(1) | 1.433(1) | 1.428(2) |
| Aryl links | | | | | |
| C–C | C(11)–C(12) 1.403(2) | C(11)–C(12) 1.407(2) | C(11)–C(12) 1.403(1) | 1.402(1) | 1.402(2) |
| | C(12)–C(13) 1.384(2) | C(12)–C(13) 1.386(2) | C(12)–C(13) 1.396(1) | 1.397(1) | 1.394(2) |
| | C(13)–C(14) 1.400(2) | C(13)–C(14) 1.397(2) | C(13)–C(14) 1.410(1) | 1.414(1) | 1.422(2) |
| | C(14)–C(15) 1.401(2) | C(14)–C(15) 1.402(2) | C(14)–C(15) 1.405(1) | 1.399(1) | 1.398(2) |
| | C(15)–C(16) 1.384(2) | C(15)–C(16) 1.390(2) | C(15)–C(16) 1.385(1) | 1.394(1) | 1.387(2) |
| | C(11)–C(16) 1.404(2) | C(11)–C(16) 1.405(2) | C(11)–C(16) 1.406(1) | 1.406(1) | 1.405(2) |
| | | | C(20)–C(21) 1.405(1) | 1.401(2) | 1.403(2) |
| | | | C(21)–C(22) 1.381(1) | 1.387(1) | 1.381(2) |
| | | | C(22)–C(23) 1.394(1) | 1.410(1) | 1.402(2) |
| | | | C(23)–C(24) 1.394(1) | 1.411(1) | 1.395(2) |
| | | | C(24)–C(25) 1.390(1) | 1.388(1) | 1.386(2) |
| | | | C(20)–C(25) 1.399(1) | 1.400(2) | 1.396(2) |
| C–X | | | C(23)–O(1) 1.366(1) | C(23)–N(4) | C(23)–S(1) |
| | | | | 1.383(1) | 1.758(1) |
| Inter-ring | | | | | |
| C–C | C(14)–C(17) 1.435(2) | C(14)–C(17) 1.437(2) | C(14)–C(18) 1.432(1) | 1.433(1) | 1.434(2) |
| | C(17)–C(18) 1.202(2) | C(17)–C(17A) 1.202(3) | C(18)–C(19) 1.203(1) | 1.205(1) | 1.204(2) |
| | C(18)–C(19) 1.436(2) | | C(19)–C(20) 1.435(1) | 1.435(1) | 1.436(2) |
| Bond Angles (°) | | | | | |
| C–C–C | C(14)–C(17)–C(18) 177.3(1) | C(14)–C(17)–C(17A) 178.2(2) | C(14)–C(18)–C(19) 176.1(1) | 175.3(1) | 178.5(1) |
| | C(17)–C(18)–C(19) 178.1(1) | | C(18)–C(19)–C(20) 177.9(1) | 176.5(1) | 177.8(1) |
| Torsion Angles (°) | | | | | |
| | N(1)–B(1)–C(11)–C(16) 56.7 | N(1)–B(1)–C(11)–C(17) 45.9 | N(1)–B(1)–C(11)–C(16) 41.0 | 47.9 | 49.3 |
| | C(13)–C(14)···C(17)–C(18)···C(19)–C(24) 11.1 | C(13)–C(14)..C(17)–C(17A)···C(14A)–C(13A) 0.0 | C(13)–C(14)···C(18)–C(19)···C(20)–C(25) 25.3 | 78.3 | 50.5 |

The similar energies for the luminescence of **2** and **3** are surprising and the reason for this is not completely clear at the moment. Similar luminescence energies of *ca.* 400 nm for **4**, **5** and **7** agree with transitions from excited states of similar energy and geometry regardless of the terminal substituent, which might perhaps be due to an unfavorable orientation of the aryl–X unit. After radiative relaxation a state of identical geometry is acquired, which relaxes to the ground state by rotational processes. In **6** the situation is different. Here the HOMO is located on the aniline part of the molecule and by electronic excitation a charge transfer to the adjacent cyanophenylene ring takes place. The comparatively small Stokes shift agrees with the lack of significant geometrical changes during this process. The situation in **8**, where in contrast to derivatives **4–7** an electron acceptor is placed in the *para*-position of the terminal ring, is different again. The absorption maximum of compound **8** ($\lambda_{abs.}$ = 300 nm in *c*-$C_6H_{12}$) is blue shifted relative to **4** by 24 nm and like compound **4** no significant solvatochromism of the absorption is observed. In cyclohexane the emission maximum of **8** is bathochromically shifted by 126 nm with respect to the absorption, whereas in **2** and in **4** the corresponding red shifts amount to only 77 nm or 83 nm, respectively. Compounds **2**, **4–8** show pronounced solvatochromism in line with large ICTs upon excitation and large dipole moments in the excited states. The largest bathochromic shift (123 nm) is observed for **4** upon going from cyclohexane to acetonitrile as the solvent. Dipole moment changes between the ground and excited state. $\Delta\mu$ were estimated following the Onsager–Lippert–Mataga model. According to a radius of 5.74 Å for the *p*-substituted molecules **4–6**, **8** $\Delta\mu$ values in the narrow range of 18.6–19.7 D were found (Table 6). This could be rationalized by emissive states of similar polarity.

It has been pointed out previously that the size of the dipole moment change $\Delta\mu$ is largely independent from the donor and acceptor strength of the substituents present in the molecule.[3n]

The quantum yields of the new benzodiazaboroles are also solvent sensitive and decrease with increasing solvent polarity. This is impressively documented for derivative **5** (R = OMe) with a quantum yield of 1.00 in *c*-$C_6H_{12}$ and only 0.04 in acetonitrile. Obviously the stabilization of the excited state favors the probability of a non-radiative decay.

As anticipated the insertion of a cyanophenylene unit into the B–C-bond of the phenylenethynyl-1,3,2-benzodiazaboroles leads to significant bathochromic shifts for the absorption and emission bands (for X = OMe: $\Delta\lambda_{abs}$ = 31 nm, $\Delta\lambda_{em}$ = 91 nm; X = SMe: $\Delta\lambda_{abs}$ = 31 nm, $\Delta\lambda_{em}$ = 59 nm; X = $NMe_2$: $\Delta\lambda_{abs}$ = 53 nm, $\Delta\lambda_{em}$ = 123 nm; solvent THF).

## DFT calculations

The geometries of compounds **2**, **4**, **6**, **8** and **9** were optimized by DFT calculations at the B3LYP/6-311G(d,p) level of theory. With the exception of **5** global minima occur when both benzene rings are co-planar, whereby the plane of the heterocycle deviates by 49.7° for **2** to 57.9° for **4**. The optimized structure of **4** exhibiting this particular interplanar angle is 48.0 kcal $mol^{-1}$ more stable than the completely planar structure. In contrast to the experimental observation (sum of angles 353.5°) the nitrogen atom of the amino

**Table 2** Photophysical data of compounds **2–8**

| | $\lambda_{max,abs}$ (nm) | $\lambda_{max,ex}$ ($cm^{-1}$) | $\varepsilon$ (L $mol^{-1}$ $cm^{-1}$) | $\lambda_{max,em}$ (nm) | $\lambda_{max,em}$ ($cm^{-1}$) | Stokes shift ($cm^{-1}$) | $\Phi_{fl}$ |
|---|---|---|---|---|---|---|---|
| **2**[a] | 303 | 32 700 | 24 300 | 380 | 26 100 | 6 600 | 0.83 |
| **2**[b] | 306 | 32 300 | 31 000 | 403 | 24 300 | 8 000 | 0.71 |
| **2**[c] | 305 | 32 500 | 35 300 | 421 | 23 300 | 9 200 | 0.46 |
| **2**[d] | 305 | 32 500 | 36 400 | 437 | 23 200 | 9 300 | 0.42 |
| **2**[e] | 305 | 32 500 | 40 900 | 438 | 23 100 | 9 400 | 0.72 |
| **2**[f] | 303 | 32 800 | 15 100 | 462 | 21 300 | 11 500 | 0.40 |
| **3**[a] | 314 | 31 900 | 8 500[g] | 386 | 25 900 | 6 000 | 1.00 |
| **3**[b] | 317 | 31 600 | 21 200 | 406 | 24 600 | 7 000 | 0.90 |
| **3**[c] | 314 | 31 900 | 33 600 | 426 | 23 500 | 8 400 | 0.40 |
| **3**[d] | 314 | 31 900 | 33 800 | 431 | 23 200 | 8 700 | 0.37 |
| **3**[e] | 317 | 31 600 | 35 200 | 444 | 22 500 | 9 100 | 0.69 |
| **3**[f] | 314 | 31 900 | 4 500[h] | 471 | 21 200 | 10 700 | 0.34 |
| **4**[a] | 324 | 30 500 | 27 500 | 407 | 24 500 | 6 000 | 0.63 |
| **4**[b] | 326 | 29 600 | 25 700 | 441 | 22 200 | 7 400 | — |
| **4**[c] | 327 | 30 200 | 25 800 | 464 | 20 900 | 9 300 | — |
| **4**[d] | 323 | 31 000 | 32 800 | 480 | 20 200 | 10 800 | — |
| **4**[e] | 327 | 30 200 | 28 200 | 487 | 20 100 | 10 100 | 0.40 |
| **4**[f] | 323 | 30 600 | 31 900 | 530 | 18 300 | 12 300 | — |
| **5**[a] | 339 | 29 300 | 13 700 | 403 | 24 700 | 4 600 | 1.00 |
| **5**[b] | 343 | 29 000 | 30 500 | 433 | 22 800 | 6 200 | 0.74 |
| **5**[c] | 340 | 29 000 | 23 800 | 455 | 21 600 | 7 400 | 0.69 |
| **5**[d] | 338 | 29 300 | 31 500 | 465 | 21 200 | 8 100 | 0.05 |
| **5**[e] | 340 | 29 200 | 29 300 | 477 | 20 600 | 8 600 | 0.60 |
| **5**[f] | 336 | 29 600 | 30 500 | 510 | 19 100 | 10 500 | 0.04 |
| **6**[a] | 380 | 26 400 | 32 400 | 403 | 24 700 | 1 700 | 1.00 |
| **6**[b] | 382 | 25 800 | 35 800 | 441 | 22 400 | 3 400 | 0.94 |
| **6**[c] | 382 | 25 700 | 27 200 | 459 | 21 600 | 4 100 | 0.55 |
| **6**[d] | 378 | 26 100 | 40 200 | 478 | 20 700 | 5 400 | 0.55 |
| **6**[e] | 380 | 25 900 | 33 900 | 476 | 20 800 | 5 100 | 0.63 |
| **6**[f] | 376 | 26 200 | 35 100 | 522 | 18 800 | 7 400 | 0.06 |
| **7**[a] | 349 | 28 500 | 35 900 | 408 | 24 400 | 4 100 | 0.77 |
| **7**[b] | 351 | 28 000 | 28 600 | 439 | 22 400 | 5 600 | 0.77 |
| **7**[c] | 349 | 28 100 | 33 300 | 462 | 21 300 | 6 800 | 0.55 |
| **7**[d] | 346 | 28 400 | 29 700 | 469 | 20 700 | 7 700 | 0.02 |
| **7**[e] | 348 | 28 400 | 39 600 | 486 | 20 200 | 8 200 | 0.55 |
| **7**[f] | 341 | 28 800 | 19 100 | 528 | 18 400 | 10 400 | 0.02 |
| **8**[a] | 300 | 31 900 | 31 200 | 426 | 23 300 | 8 600 | 0.60 |
| **8**[b] | 301 | 31 200 | 24 000 | 470 | 21 000 | 10 200 | 0.49 |
| **8**[c] | 301 | 31 500 | 33 900 | 497 | 19 800 | 11 700 | 0.34 |
| **8**[d] | 300 | 30 700 | 33 900 | 525 | 18 500 | 12 200 | 0.16 |
| **8**[e] | 302 | 31 400 | 34 000 | 530 | 18 500 | 12 900 | 0.13 |
| **8**[f] | 298 | — | 15 100 | — | — | — | — |

Solvents[a] cyclohexane, [b] toluene, [c] $CHCl_3$, [d] THF, [e] $CH_2Cl_2$, [f] MeCN. [g] Small value is due to poor solubility in $c$-$C_6H_{12}$. [h] Small value is due to partial decomposition in $CH_3CN$ into non-fluorescing fragments.

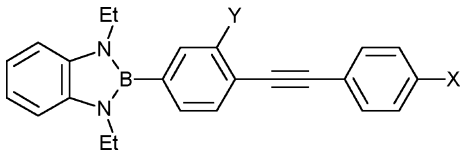
group in **6** is planar (sum of angles 359.2°). This plane is slightly twisted out of the adjacent benzene plane as is evident from the torsion angles of 5.5° and 4.9°. In the experimentally determined structure this angle was measured as 24.4°. Thus, according to the calculation, a maximum π-delocalization of the amino group and arene ring is observed. Table 3 lists selected geometrical parameters for **2**, **4–6** and **8**. Comparison of the experimental by determined bond lengths and angles and the optimized geometries reveal very good agreement. The calculations and the X-ray studies differ, however, in the mutual orientation of the ring planes.

The calculated absorption maxima from TD–DFT computations on the compounds clearly depend on the mutual orientation of all three rings (Table 4). These absorptions arise from low energy HOMO–LUMO transitions. In comparison to the experiment, the measured absorption values for **2**, **4–6**, **8** (in $c$-$C_6H_{12}$) are red shifted by 3–32 nm, which may be rationalized by the presence of all conformers in the solvent. In the gas phase, planarity between the arene units and the absence of solvent favors long wave absorptions. In contrast, the calculated absorption maximum of **3** is blue shifted by 4 nm.

Table 5 lists the HOMO–LUMO gaps and the molecular orbitals for compounds **2–6**, **8** and **9**. In derivatives **2–5** and **8** the HOMOs correspond to the antibonding interaction $\pi_3$–$\pi_{NBN}$ inside the benzodiazaborole ring. The LUMO for all species under investigation has no orbital contributions from the diazaborole unit, leading to HOMO–LUMO gaps varying from 5.72 eV in **8** (X = CN, Y = CN) to 6.39 eV in **2** (X = H, Y = H). Substitution of the 3-position in the central ring of **3** by the electron-withdrawing cyano function affords derivative **9** whereby the symmetry of the molecule is broken. As a consequence the orbital $[\pi_3$–$\pi_{NBN}]^+$ is no longer the HOMO of the resulting species, but the HOMO-1. The HOMO of **9** is the antibonding combination $\pi_3$–$\pi_{NBN}$ inside the benzodiazaborole ring at the position X of the terminal benzene ring.

Similarly, the introduction of the cyano group into molecule **3** leads to a narrowing of the HOMO–LUMO gap from 6.24 to

**Table 3** Selected bond lengths [Å] and angles [°] calculated [B3LYP/6-311G(d,p)] for optimized geometries of **2**, **4–6** and **8**




| | **2** | **4** | **5** | **6** | **8** |
|---|---|---|---|---|---|
| | X = Y = H | X = H, Y = CN | X = OMe, Y = CN | X = $NMe_2$, Y = CN | X = Y = CN |
| Bond lengths (Å) | | | | | |
| B–C | 1.565 | 1.568 | 1.568 | 1.565 | 1.568 |
| B–N | 1.442 | 1.439 | 1.443 | 1.441 | 1.439 |
| C–N | 1.397 | 1.398 | 1.398 | 1.392 | 1.398 |
| C≡C | 1.211 | 1.210 | 1.210 | 1.212 | 1.210 |
| C–C(≡C) | 1.423 | 1.420 | 1.418 | 1.415 | 1.418 |
| C–X | 1.084 | 1.084 | 1.360 | 1.373 | 1.430 |
| Bond angles (°) | | | | | |
| N–B–N | 106.2 | 106.2 | 106.2 | 106.2 | 106.6 |
| B–N–C | 108.6 | 108.2 | 108.3 | 108.2 | 108.1 |
| N–B–C | 126.9 | 126.8 | 126.9 | 126.8 | 126.7 |
| C–C≡C | 180.0 | 178.5 | 178.0 | 178.4 | 178.2 |
| Torsion angles (°) | | | | | |
| N–B–C–C | 49.7 | 57.1 | 51.9 | 50.0 | 49.8 |
| C═C–(≡)–C═C | 0.0 | 1.1 | 19.4 | 0.9 | 0.3 |

**Table 4** Comparison of calculated [B3LYP/6-311G(d,p)] data for optimized geometries of **2–6**, **8** and **9** and observed UV absorption maxima (in *c*-$C_6H_{12}$)

| Compound | $\lambda_{max(calcd)}$ (nm) | Oscillator (calcd) strength (f) | $\lambda_{max}$ (exp, nm) | $\Delta\lambda_{max}$ (calcd – exp) |
|---|---|---|---|---|
| **2** | 307 | 0.92 | 303 | +4 |
| **3** | 310 | 1.09 | 314 | –4 |
| **4** | 327 | 0.55 | 324 | +3 |
| **5** | 360 | 0.54 | 339 | +21 |
| **6** | 390 | 1.10 | 380 | +10 |
| **8** | 332 | 1.14 | 300 | +32 |
| **9** | 330 | 0.59 | — | — |

5.93 eV. The stabilization of the HOMO of **3** from –6.82 to –6.93 eV is much less pronounced than that of the LUMO from –0.59 to –1.00 eV. In going from **2** to **4** the introduction of the CN-function leads to a narrowing of the HOMO–LUMO gap from 6.40 to 6.13 eV. The situation is different for the dimethylamino derivative **6**.

Due to the rather strong π-donor effect of the amino group the orbital $\pi_{C\equiv C}{}^{\pi}$–$\pi_2$(Ph″)–$n_N{}^{\pi}$(X) is considerably stabilized and corresponds to the HOMO of this system, while the MO $\pi_3$–$\pi_{NBN}$ now becomes the HOMO-1. Here it has to be noted that CAM-B3LYP/6-311G(d,p) tends to overestimate HOMO–LUMO gaps.

With regard to the nature of the frontier orbitals in compound **8** the UV-absorption induces an intramolecular charge-transfer transition from the benzodiazaborolyl group into the LUMO of the molecule which is virtually located at the terminal *p*-cyanophenylene–ethynyl unit.

In the UV-spectrum of **2** the low energy absorption was attributed to the ICT transition from the benzodiazaborole ring to the central phenylene (ethynylene) unit. Similar ICT transitions occur in **4** and **5** by UV excitation. Due to the different situation in the frontier orbitals of the dimethylamino derivative **6** the HOMO–LUMO transition is described as an ICT from the electron-releasing aminophenyl group into the CN-functionalized part of the scaffold. The dipole moment has also changed its direction from the ground to the excited state.

The ground state dipole moments $\mu_g$, molecular polarizabilities $\alpha$ and the static first hyperpolarizabilities $\beta$ of compounds **2–6**, **8** and the hypothetical molecule **9** have been calculated using the two state model[18] and are listed in Table 7. The magnitudes of $\mu_g$ are all found to be rather small and depend on the substituents on the terminal aryl ring. They range from 1.1 D for the cyano-free derivative **2**, *via* 3.5 D for the CN-side group containing **4** to 7.5 D for **8**, where the donating benzodiazaborole group and the terminal CN-acceptor are ideally separated. These low values are consistent with only a little charge transfer in the ground state of the compounds. The electronic transitions upon excitation were accompanied by significant charge transfer processes as evident from the pronounced solvatochromism of the emissions and the experimentally derived change of the dipole moment of 14.8–19.7 D.

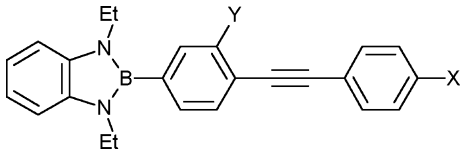
The molecular polarizabilities $\alpha$ of compounds **4–8** featuring CN-side groups vary little in the range $5.3–6.2 \times 10^{-23}$ esu. The $\alpha$-values for derivatives **3** and **9** are $7.6 \times 10^{-23}$ esu and $7.9 \times 10^{-23}$ esu, which suggests that a second benzodiazaborole unit at the terminus of the rod-like molecule confers more to its polarizability than the remaining substituents in this study.

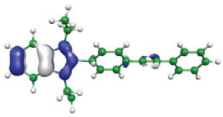
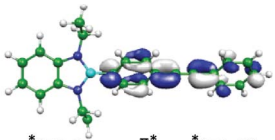
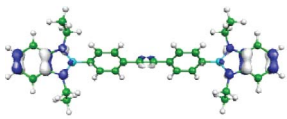
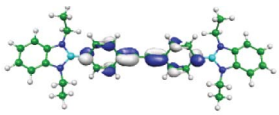
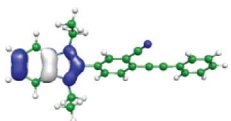
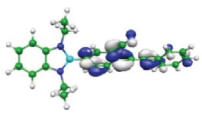
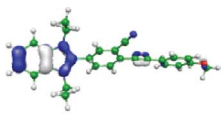
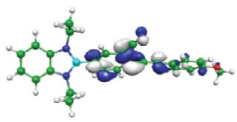
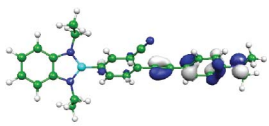
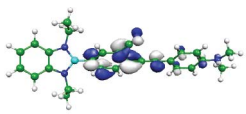
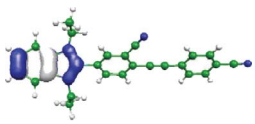
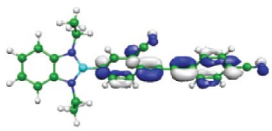
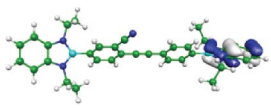
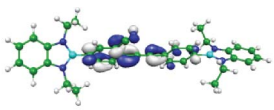
In compounds of the type $Mes_2B–C\equiv C–C_6H_4–4–R$ the polarizabilities $\alpha$ vary between $4.4 \times 10^{-23}$ esu (R = H) and $5.0 \times 10^{-23}$ esu, except for $Mes_2B–C\equiv C–C_6H_4–4–NO_2$, where $\alpha = 8.8 \times 10^{-23}$ esu were found.[8]

Donor/acceptor substituted π-conjugated organic molecules having low-lying charge transfer excited states exhibit large first-order non-linear properties. The molecular hyperpolarizabilities $\beta$ of **2–6**, **8** and **9** were computed as analytical third derivatives of the energy and correspond to the static hyperpolarizabilities (frequency = 0). An increase in the range $\beta = 5.0 \times 10^{-30}$ esu (**2**) ≤ $5.6 \times 10^{-30}$ esu (**4**) < $21.1 \times 10^{-30}$ esu (**8**) < $33.8 \times 10^{-30}$ esu (**5**) ≪ $76.8 \times 10^{-30}$ esu (**6**) was calculated. An interpretation of these data

**Table 5** Calculated [CAM-B3LYP/6-311G(d,p)] HOMO–LUMO gaps and MO nature of **2–6**, **8** and **9** (BDB = 1,3-diethyl-1,3,2-benzodiazaborolyl). Contour values are plotted at ±0.04 e bohr$^{-3})^{1/2}$




| | X | Y | HLG | HOMO | LUMO |
|---|---|---|---|---|---|
| **2** | H | H | 6.40 |  -6.86 $\pi_3$-$\pi_{NBN}$ |  -0.47 $\pi_2^*$(Ph′)-$\pi_{C\equiv C}^{\pi^*}$-$\pi_2^*$(Ph″) |
| **3** | BDB | H | 6.24 |  -6.82 $[\pi_3$-$\pi_{NBN}]^+$ |  -0.58 $\pi_2^*$(Ph′)-$\pi_{C\equiv C}^{\pi^*}$-$\pi_2^*$(Ph″) |
| **4** | H | CN | 6.13 |  -7.10 $\pi_3$-$\pi_{NBN}$ |  -0.97 $\pi_2^*$(Ph′)-$\pi_{C\equiv N}^{\pi^*}$-$\pi_{C\equiv C}^{\pi^*}$-$\pi_2^*$(Ph″) |
| **5** | OMe | CN | 6.16 |  -6.99 $\pi_3$-$\pi_{NBN}$ |  -0.83 $\pi_2^*$(Ph′)-$\pi_{C\equiv N}^{\pi^*}$-$\pi_{C\equiv C}^{\pi^*}$-$\pi_2^*$(Ph″) |
| **6** | $NMe_2$ | CN | 5.82 |  -6.51 $\pi_{C\equiv C}^{\pi}$-$\pi_2$(Ph″)-$n_N^{\pi}$(X) |  -0.69 $\pi_2^*$(Ph′)-$\pi_{C\equiv N}^{\pi^*}$-$\pi_{C\equiv C}^{\pi^*}$-$\pi_2^*$(Ph″) |
| **8** | CN | CN | 5.72 |  -7.24 $\pi_3$-$\pi_{NBN}$ |  -1.52 $\pi_2^*$(Ph′)-$\pi_{C\equiv N}^{\pi^*}$-$\pi_{C\equiv C}^{\pi^*}$-$\pi_2^*$(Ph″) |
| **9** | BDB | CN | 5.93 |  -6.93 ($\pi_3$-$\pi_{NBN}$) X |  -1.00 $\pi_2^*$(Ph′)-$\pi_{C\equiv N}^{\pi^*}$-$\pi_{C\equiv C}^{\pi^*}$-$\pi_2^*$(Ph″) |

on the basis of the two state model, whereby $\beta$ is proportional to the dipole moment change between the ground and the excited state $\Delta\mu$ and the square of the transition moment integral for the optical transition between two states (oscillator strength). Moreover, the hyperpolarizability is inversely proportional to the square of the energy of the respective transition (HOMO–LUMO gap). According to the Lippert–Mataga model $\Delta\mu$ does not change significantly (*ca.* 19 D), and with the exception of **4** and **5** ($f$ = 0.55) the oscillator strength for the remaining derivatives is *ca.* 1. As observed with donor/acceptor functionalized tolanes

**Table 6** CAM-B3LYP/6-311G+(d,p) calculated ground state ($\mu_g$) dipole moments, molecular polarizabilities ($\alpha$), static first-order molecular hyperpolarizabilities ($\beta$) and experimental change of dipole moments ($\Delta\mu$) of compounds **2–6**, **8** and **9**

| Compound | $\mu_g$ [D] | $\alpha$ [$10^{-23}$ esu] | $\beta$ [$10^{-30}$ esu] | $\Delta\mu$ [D] |
|---|---|---|---|---|
| **2** | 1.1 | 5.1 | 5.0 | 14.8 |
| **3** | 0.0 | 7.6 | 0.0 | — |
| **4** | 3.5 | 5.3 | 5.6 | 19.7 |
| **5** | 4.7 | 5.7 | 33.8 | 18.9 |
| **6** | 4.7 | 6.2 | 76.8 | 19.4 |
| **8** | 7.5 | 5.7 | 21.1 | 18.6 |
| **9** | 3.9 | 7.9 | 22.6 | — |

4-D-$C_6H_4$–C≡C–$C_6H_4$-4-A [3m] or arylethynyl-dimesityl-boranes 4-D-$C_6H_4$–C≡C–$BMes_2$[8] the magnitude of $\beta$ in **2**, **4–8** may also be dominated by the size of the HOMO–LUMO gaps (reflecting the donor/acceptor strengths). Ordering schemes for $\beta$ by the donor/acceptor strengths, however, are at best approximate as various donor–acceptor pairs couple differently across the conjugated framework. In keeping with this, the large $\beta$-value of **6** ($76.8 \times 10^{-30}$ esu) would agree with a small HOMO–LUMO gap (5.82 eV), an oscillator strength of 1.10 and a $\Delta\mu$ of 19.4 D. Here, however, as pointed out before, the ICT transition reflects the donation of charge from the electron rich dimethylaminoaryl ring onto the central cyanophenyl ring, which differs from all remaining derivatives in this study. In **8** the ICT transition from the benzodiazaborole to the terminal cyanophenyl acceptor has a similar oscillator strength ($f$ = 1.14), a similar $\Delta\mu$ (= 18.6 D) and an even smaller HOMO–LUMO gap than **6**. Against intuition a $\beta$-value of only $21.1 \times 10^{-30}$ esu was calculated for **8**. For compound **5** the hyperpolarizability $\beta$ was computed to be $33.8 \times 10^{-30}$ esu, even though the HOMO–LUMO gap (6.17 eV) and the oscillator strength of 0.54 are smaller than in **8** and $\Delta\mu$ is similar (18.6 D). Anyway, our results are virtually consistent with observations by Marder and others[8] that a large charge transfer upon excitation leads to higher dipole moments, pronounced solvatochromism and significant NLO activities. Thereby, hyperpolarizabilities $\beta$ of molecules $Mes_2B$–C≡C–$C_6H_4$-4-R range from $2.5 \times 10^{-30}$ to $25.7 \times 10^{-30}$ esu.

## Conclusion

It has been demonstrated that 1,3,2-benzodiazaboroles, functionalized by variously substituted diphenylacetylenes have been synthesized using known methodologies. Unlike their absorption maxima, their emission maxima are characterized by large solvatochromic shifts in solvents of increasing polarity, which is indicative of significant dipole moments in the excited state. Using the Onsager–Lippert–Mataga approximation changes of the dipole moment between the ground state and the excited state of *ca.* 19 D for the cyano substituted derivatives were estimated. Static first-order molecular hyperpolarisibilities $\beta$ for the novel compounds range from $5.0 \times 10^{-30}$ to $76.8 \times 10^{-30}$ esu. A straightforward explanation for these data, however, could not be obtained on the basis of the familiar two-state model.

## Experimental

All experiments were performed under dry, oxygen-free argon by using standard Schlenk technique. Solvents were dried with appropriate drying agents and freshly distilled under argon before use. The following compounds were prepared according

**Table 7** Crystal data for **2**, **3**, **5**, **6** and **7**

| | **2** | **3** | **5** | **6** | **7** |
|---|---|---|---|---|---|
| Empirical formula | $C_{24}H_{23}BN_2$ | $C_{34}H_{36}B_2N_4$ | $C_{26}H_{24}B_3N_3O$ | $C_{27}H_{27}BN_4$ | $C_{26}H_{24}BN_3S$ |
| M [g mol$^{-1}$] | 350.25 | 522.29 | 405.29 | 418.34 | 421.35 |
| Crystal dimensions (mm) | 0.30 × 0.25 × 0.20 | 0.22 × 0.14 × 0.06 | 0.30 × 0.28 × 0.24 | 0.30 × 0.21 × 0.10 | 0.30 × 0.27 × 0.20 |
| Crystal system | Triclinic | Monoclinic | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ [Å] | 8.2289(1) | 9.8599(3) | 7.6596(2) | 8.1333(3) | 10.1351(2) |
| $b$ [Å] | 935640(1) | 11.9000(4) | 8.2312(1) | 8.8483(2) | 10.7913(2) |
| $c$ [Å] | 26.2207(3) | 12.5138(3) | 18.3644(3) | 15.7389(5) | 10.8348(2) |
| $\alpha$ [°] | 90.276(1) | 90 | 100.449(1) | 92.105(2) | 82.583(1) |
| $\beta$ [°] | 94.182(1) | 103.875(2) | 90.037(1) | 94.804(2) | 73.105(1) |
| $\gamma$ [°] | 102.184(1) | 90 | 108.983(1) | 91.021(2) | 80.018(1) |
| $V$ [Å$^3$] | 1967.66(4) | 1425.44(7) | 1074.49(4) | 1127.68(6) | 1112.80(4) |
| $Z$ | 4 | 2 | 2 | 2 | 2 |
| $\varsigma_{calc}$ [g cm$^{-1}$] | 1.182 | 1.217 | 1.253 | 1.232 | 1.257 |
| $\mu$ [mm$^{-1}$] | 0.068 | 0.071 | 0.077 | 0.073 | 0.164 |
| $F$ (000) | 744 | 556 | 428 | 444 | 444 |
| $\Theta$ [°] | 3–27.5 | 3–27.5 | 3–27.5 | 3–30.1 | 3.4–25.0 |
| No refl. collected | 39445 | 19844 | 24875 | 22633 | 22441 |
| No refl. unique | 9002 | 3195 | 4894 | 6329 | 3882 |
| $R$ (int) | 0.033 | 0.042 | 0.028 | 0.029 | 0.026 |
| No refl. [$I > 2\sigma(I)$] | 7048 | 2625 | 4247 | 5322 | 3612 |
| Refined parameters | 491 | 183 | 283 | 293 | 376 |
| GOF | 1.046 | 1.046 | 1.058 | 1.022 | 1.075 |
| $R_f$ [$I > 2\sigma(I)$] | 0.0394 | 0.0428 | 0.0379 | 0.0430 | 0.0301 |
| $wR_F2$ (all data) | 0.1016 | 0.1116 | 0.1018 | 0.1156 | 0.0785 |
| $\Delta\varsigma_{max/min}$ [e Å$^{-3}$] | 0.243/–0.215 | 0.249/–0.249 | 0.271/–0.267 | 0.312/–0.232 | 0.258/–0.255 |
| CCDC number | 780599 | 780600 | 780601 | 780602 | 780603 |

to literature procedures: 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (**1**),[16] 4-bromo-diphenylacetylene,[15] 5-bromo-2-{[4-(methoxy)phenyl]ethynyl}benzonitrile,[6] 5-bromo-2-{[4-(dimethylamino)phenyl]ethynyl}benzonitrile,[6] 5-bromo-2-{[4-(methylthio)phenyl]ethynyl}benzonitrile,[6] 5-bromo-2-[(4-cyanophenyl)-ethynyl]benzonitrile,[6] bis(4-bromophenyl)acetylene,[17] 2-bromo-5-iodobenzonitrile.[15] 4-Bromophenylacetylene, 4-methoxyphenylacetylene, 1,4-bromoiodobenzene, trimethylsilylacetylene, $[(Ph_3P)_2PdCl_2]$ and CuI were purchased commercially.

### 1,3-Diethyl-2[4′-phenylethynyl]phenyl-1,3,2-benzodiazaborole (2)

A stirred THF solution (50 mL) of 4-bromodiphenylacetylene (0.55 g, 2.14 mmol) was combined dropwise at −78 °C with 2.26 mmol *n*-butyllithium dissolved in 1.41 mL of *n*-hexane. Stirring at this temperature was continued for 30 min. Then the dry ice bath was removed and the reaction mixture was stirred for 30 min at 20 °C. After re-cooling to −78 °C a sample of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (**1**) (0.54 g, 2.14 mmol) was added. Stirring at −78 °C was pursued for 1 h, and then overnight at room temperature. The mixture was evaporated to dryness, the residue triturated with dichloromethane (20 mL) and the obtained slurry was filtered. Solvent and volatile components were removed from the filtrate *in vacuo*, the off-white crude product was then washed with *n*-pentane (2 × 5 mL, 0 °C) before it was crystallized from a dichloromethane–*n*-hexane mixture. Compound **2** was obtained as colorless crystals in 39% yield.

Found C 80.27, H 6.85, N 8.46%; $C_{24}H_{23}BN_3$ requires C 82.20, H 6.62, N 8.00%; repeated experiments did not provide improved C-values. Obviously, boron carbide formation has led to incomplete combustion of the compound. $^1$H-NMR ($CDCl_3$): $\delta$ = 1.31 (t, $J_{HH}$ = 7.2 Hz, 6H, $CH_2CH_3$), 3.78 (q, $J_{HH}$ = 7.2 Hz, 4H, $CH_2CH_3$), 7.08 (m, 5H, H–Ph, H-borole), 7.35 (m, 4H, H–Ph, H-borole), 7.55 (d, $J_{HH}$ = 7.6 Hz, 2H, H–Ph), 7.61 (d, $^3J_{HH}$ = 7.6 Hz, H–Ph) ppm; $^{13}$C-{$^1$H}-NMR ($CDCl_3$): $\delta$ = 16.3 (s, $CH_2CH_3$), 37.6 (s, $CH_2CH_3$), 89.5, 90.0 (2, s, C≡C), 108.9 (s, *C*H–CH=CH–*C*H, borole), 118.7 (s, CH=*C*H–*C*H=CH, borole), 123.3 (s), 133.4 (s, C–Ph), 137 (s, $C_2N_2$) ppm; $^{11}$B-{$^1$H}-NMR ($CDCl_3$): $\delta$ = 28.6 (s) ppm; MS–EI (*m*/*z*): 350.2 [$M^+$].

### 4,4′-Bis[2″-1″,3″-diethyl-1″,3″,2″-benzodiazaborolyl]-diphenylacetylene (3)

A solution of bis(4-bromophenyl)acetylene (0.51 g, 1.53 mmol) in 40 mL of THF was treated at −78 °C with 2.15 mL (3.44 mmol) of a 1.6 M solution of *n*-butyllithium in *n*-hexane. After stirring for 30 min at −78 °C the reaction mixture was warmed up to 20 °C and stirred for another 30 min. Re-cooling to −78 °C was followed by the addition of 2-bromo-1,3,2-benzodiazaborole (**1**) (0.80 g, 3.17 mmol). After stirring the chilled solution for 1 h and warming to room temperature it was stirred over night. Solvent and volatile components were removed *in vacuo*, the residue stirred with 30 mL of dichloromethane and filtered. The filtrate was liberated from volatiles and the solid residue was purified by short-path distillation at $10^{-6}$ bar and 300 °C. The light yellow solid distillate was crystallized from methylcyclohexane–dichloromethane to afford product **3** as colorless yellow rods (yield: 0.38 g, 48%).

$^1$H-NMR ($CDCl_3$): $\delta$ = 1.32 (t, $J_{HH}$ = 7.2 Hz, 12H, $CH_2CH_3$), 3.79 (q, $J_{HH}$ = 7.2 Hz, 8H, $CHCH_3$), 7.06 (m, 4H, C*H*=CH–CH=C*H*), 7.13 (m, 4H, CH=C*H*–C*H*=CH), 7.57 (d, $J_{HH}$ = 7.5 Hz, H–Ph), 7.64 (d, $J_{HH}$ = 7.5 Hz, H–Ph) ppm; $^{13}$C-{$^1$H}-NMR ($CDCl_3$): $\delta$ = 16.3 (s, $CH_2CH_3$), 37.7 (s, $CH_2CH_3$), 90.2 (s, C≡C), 109 (s, *C*H–CH=CH–*C*H), 118.8 (s, CH=*C*H–*C*H=CH), 123.4 (s), 131.1 (s), 133.4 (s), 133.7 (s, C–Ph), 137.1 (s, $C_2N_2$) ppm; $^{11}$B-{$^1$H}-NMR ($CDCl_3$): $\delta$ = 28.5 (s) ppm; MS–EI (*m*/*z*): 522.3 [$M^+$].

### 2[3′-Cyano-4′[phenylethynyl]phenyl]-1,3-diethyl-1,3,2-benzodiazaborole (4)

A sample of an 1.6 M solution of *n*-butyllitium (2.4 mL, 3.9 mmol) in *n*-hexane was slowly added to chilled solution (−110 °C) of 5-bromo-2-(phenylethynyl)benzonitrile (1.1 g, 3.9 mmol) in 40 mL of THF. After stirring for 20 min a solution of **1** (0.98 g, 3.9 mmol) in THF (10 mL) was added dropwise. Stirring the resulting mixture at −110 °C was continued for 4 h. Then it was allowed to slowly warm up to room temperature. After 16 h of stirring the solution was evaporated to dryness. The solid residue was suspended in 30 mL of *n*-hexane, heated to *ca.* 60 °C and filtered while still hot. The filter-cake was extracted with 20 mL of hot *n*-hexane. The combined filtrates were freed from solvent and volatile components *in vacuo*, and the solid residue was purified by crystallization from *n*-hexane at −35 °C. The crude product **4** was obtained as a dark green powder (1.14 g, 78%). The green impurity was removed by dissolving the powder in diethylether and slowly cooling to −35 °C (0.81 g, 55% yield).

Found C 79.20, H 5.92, N 11.20%; $C_{22}H_{22}BN_2$ requires C 80.01, H 5.91, N 11.20%; $^1$H-NMR ($C_6D_6$): $\delta$ = 0.96 (t, $J_{HH}$ = 7.2 Hz, 6H, $CH_2CH_3$), 3.33 (q, $J_{HH}$ = 7.2 Hz, 4H, $CH_2CH_3$), 6.98 (m, 3H, H–Ph and 2H, C*H*=CH–CH=C*H*), 7.15 (m, 2H, CH=C*H*–C*H*=CH), 7.22 (dd, $J_{HH}$ = 7.6, 2.2 Hz, 1H, H-benzonitrile), 7.32 (d, $J_{HH}$ = 7.6 Hz, 1 Hz, 1H, H-benzonitrile), 7.46 (d, $J_{HH}$ = 2.2 Hz, 1H, H-benzonitrile), 7.64 (m,2H, H–Ph) ppm; $^{13}$C-{$^1$H}-NMR ($C_6D_6$): $\delta$ = 16.0 (s, $CH_2CH_3$), 37.4 (s, $CH_2CH_3$), 86.4, 96.6 (2 s, C≡C), 109.4 (s, *C*H=CH–CH=*C*H), 115.8 (s, *C*–CN), 117.8 (s, C–*C*N), 119.5 (s, CH=*C*H–*C*H=CH), 122.3 (s, C–Ph), 127.1 (s, C-benzonitrile), 128.6 (s, *m*-CH–Ph), 129.2 (s, *p*-CH–Ph), 131.3 (s, CH-benzonitrile), 132.2 (s, *o*-CH–Ph), 136.7 (s, CH-benzonitrile), 137.0 (s, $C_2N_2$), 137.3 (s, CH-benzonitrile); $^{11}$B-{$^1$H}-NMR ($C_6D_6$): $\delta$ = 27.45 (s) ppm; MS–EI (*m*/*z*): 375.1 [$M^+$].

### 2[3′-Cyano-4′[4″-methoxyphenylethynyl]phenyl]-1,3-diethyl-1,3,2-benzodiazaborole (5)

The solution of 5-bromo-2-{[4-(methoxy)phenyl]ethynyl}-benzonitrile (2.0 g, 6.4 mmol) in THF (50 mL) was cooled to −110 °C, and was then slowly combined with 6.7 mmol *n*-butyllitium (4.2 mL, 1.6 M in *n*-hexane). Stirring at −110 °C was continued for 1 h before a THF solution (5 mL) of **1** (1.87 g, 6.4 mmol) was added dropwise. The resulting mixture was stirred for 5 h at −110 °C and then warmed up to room temperature. During warm-up the solvent was removed *in vacuo*. The green–brown residue was suspended in 40 mL of dichloromethane and filtered. The filtrate was stored for 12 h at −20 °C, whereby light brown crystals separated. The supernatant solution was decanted and the crystals were washed with 2 mL of cold dichloromethane.

Recrystallization from *n*-hexane–dichloromethane yielded 0.89 g (38%) of **5** as colorless crystals.

Found C 76.78, H 5.92, N 10.45%; $C_{26}H_{24}BN_3O$ requires C 77.05, H 5.97, N 10.37%; $^1$H-NMR ($C_6D_6$): $\delta$ = 0.96 (t, $J_{HH}$ = 7.2 Hz, 6H, $CH_2CH_3$), 3.17 (s, 3H, $OCH_3$), 3.34 (q, $J_{HH}$ = 7.2 Hz, 4H, $CH_2CH_3$), 6.58 (d, $J_{HH}$ = 8.8 Hz, 2H, $CH_3O$–C=C*H*), 6.97 (m, 2H, C*H*=CH–CH=C*H*), 7.15 (m, 2H, CH=C*H*–C*H*=CH), 7.25 (dd, $J_{HH}$ = 7.7, 1.3 Hz, 1H, H-benzonitrile), 7.38 (d, $J_{HH}$ = 7.7 Hz, 1H, H-benzonitrile), 7.49 (d, $J_{HH}$ = 1.3 Hz, H-benzonitrile), 7.61 (d, $J_{HH}$ = 8.8 Hz, 2H, $CH_3O$–C=CH–C*H*); $^{13}$C{$^1$H}-NMR ($C_6D_6$): $\delta$ = 16.0 (s, $CH_2CH_3$), 37.4 (s, $CH_2CH_3$), 54.6 (s, $OCH_3$), 85.9, 97.6 (2 s, C≡C), 109.4 (s, *C*H=CH–CH=*C*H), 114.3 (s, C–Ph), 114.4 (s, $H_3CO$–C=*C*H), 115.6 (s, *C*–CN), 117.9 (s, C–*C*N), 119.5 (s, CH=*C*H–*C*H=CH), 127.6 (s, C-benzonitrile), 131.0 (s, CH-benzonitrile), 133.8 (s, $H_3CO$–C=CH–*C*H), 136.7 (s, CH-benzonitrile), 137.0 (s, $C_2N_2$), 137.3 (s, CH-benzonitrile), 160.7 (s, *C*–$OCH_3$); $^{11}$B{$^1$H}-NMR ($C_6D_6$): $\delta$ = 27.4 (s); MS–EI (*m*/*z*): 405.2 [M$^+$].

### 2[3′-Cyano-4′[4″-(dimethylamino)phenylethynyl]phenyl]-1,3-diethyl-1,3,2-benzodiazaborole (6)

The solution of 5-bromo-2-{[4-(dimethylamino)phenyl]-ethynyl}benzonitrile (0.88 g, 7.71 mmol) in THF (40 mL) was chilled to −110 °C before 1.7 mL (2.72 mmol) of a 1.6 M solution of *n*-butyllithium in *n*-hexane were added dropwise. The mixture was stirred at −110 °C for 30 min. Then a solution of 2-bromo-1,3,2-benzodiazaborole (**1**) (1.87 g, 6.4 mmol) in 5 mL of THF was added dropwise. The solution was allowed to reach room temperature within 2 h, and then stirred overnight. Solvent and volatile component were completely removed *in vacuo*. The resulting residue was extracted with *n*-hexane during a period of 4 d. A green microcrystalline solid separated from the extract. It was filtered and the filter-cake was dried *in vacuo* and then recrystallized from THF to give product **6** as light yellow crystals (yield: 0.80 g, 71%).

Found C 77.30, H 6.37, N 13.43%; $C_{27}H_{27}BN_4$ requires C 77.52, H 6.51, N 13.39%; $^1$H-NMR ($CDCl_3$): $\delta$ = 1.34 (t, $J_{HH}$ = 7.2 Hz, 6H, $CH_2CH_3$), 3.02 (s, 6H, $N(CH_3)$), 3.79 (q, $J_{HH}$ = 7.2 Hz, 4H, $CH_2CH_3$), 6.86 (d, $J_{HH}$ = 8.8 Hz, 2H, $(CH_3)_2N$–C=C*H*–CH), 7.09 (m, 2H, C*H*=CH–CH=C*H*), 7.16 (m, 2H, CH=C*H*–C*H*=CH), 7.54 (d, $J_{HH}$ = 8.8 Hz, 2H, $(CH_3)_2N$–C=CH–C*H*), 7.66 (d, $J_{HH}$ = 7.9 Hz, 1H, H-benzonitrile), 7.72 (dd, $J_{HH}$ = 7.9, 1.3 Hz, 1H, H-benzonitrile), 7.84 (d, $J_{HH}$ = 1.3 Hz, H-benzonitrile); $^{13}$C{$^1$H}-NMR ($CDCl_3$) $\delta$ = 15.3 (s, $CH_2CH_3$), 36.6 (s, $CH_2CH_3$), 39.1 (s, $N(CH_3)_2$), 83.6 (s, C-acetylene), 97.8, 107.4 (s, C≡C), 107.4 (s, C–Ph), 108.1 (s, *C*H=CH–CH=*C*H), 110.6 (s, $(H_3C)_2N$–C=*C*H), 113.3 (s, *C*–CN), 117.2 (s, C–*C*N), 118.1 (s, CH=*C*H–*C*H=CH), 127.2 (s, C-benzonitrile), 129.9 (s, CH-benzonitrile), 132.3 (s, $(H_3C)_2N$–C=CH–*C*H), 135.8 (s, $C_2N_2$), 136.0 (s, CH-benzonitrile), 136.2 (s, CH-benzonitrile), 149.7 (s, *C*–$N(CH_3)_2$); $^{11}$B{$^1$H}-NMR ($CDCl_3$): $\delta$ = 27.6 (s); MS–EI (*m*/*z*): 418.3 [M$^+$].

### 2[3′-Cyano-4′[4″-(methylthio)phenylethynyl]phenyl]-1,3-diethyl-1,3,2-benzodiazaborole (7)

Analogously the chilled solution (−110 °C) of 5-bromo-2-{[4-(methylthio)phenyl]ethynyl}benzonitrile (0.91 g, 2.77 mmol) in THF (25 mL) was combined with a 1.6 M *n*-butyllithium solution in *n*-hexane (1.75 mL, 2.8 mmol) and after 20 min at the same temperature a THF solution (5 mL) of 0.70 g (2.77 mmol) **1** was added. After an analogous workup (16 h, extraction of the residue with *n*-$C_6H_{14}$) a microcrystalline light red solid was separated. Recrystallization from $CHCl_3$ furnished 0.81 g (69%) of colorless crystalline **7**.

Found C 73.58, H 5.70, N 9.80, S 7.32%;$C_{26}H_{24}BN_3S$ requires C 74.11, H 5.74, N 9.97, S 7.61%; $^1$H-NMR ($C_6D_6$): $\delta$ = 0.97 (t, $J_{HH}$ = 7.2 Hz, 6H, $CH_2CH_3$), 1.85 (s, 3H, $SCH_3$), 3.35 (q, $J_{HH}$ = 7.2 Hz, 4H, $CH_2CH_3$), 6.86 (d, $J_{HH}$ = 8.5 Hz, 2H, $CH_3S$–C=C*H*–CH), 6.98 (m, 2H, C*H*=CH–CH=C*H*), 7.15 (m, 2H, CH=C*H*–C*H*=CH), 7.25 (dd, $J_{HH}$ = 7.8, 1.3 Hz, 1H, H-benzonitrile), 7.37 (d, $J_{HH}$ = 7.8 Hz, 1H, H-benzonitrile), 7.48 (d, $J_{HH}$ = 1.3 Hz, H-benzonitrile), 7.49 (d, $J_{HH}$ = 8.5 Hz, 2H, $CH_3S$–C=CH–C*H*); $^{13}$C{$^1$H}-NMR ($C_6D_6$) $\delta$ = 14.3 (s, $SCH_3$), 16.0 (s, $CH_2CH_3$), 37.5 (s, $CH_2CH_3$), 86.5, 97.6 (2 s, C≡C), 109.4 (s, *C*H=CH–CH=*C*H), 115.7 (s, *C*–CN), 117.9 (s, C–*C*N), 118.1 (s, C–Ph), 119.5 (s, CH=*C*H–*C*H=CH), 125.7 (s, $H_3CS$–C=*C*H), 127.3 (s, C-benzonitrile), 131.0 (s, CH-benzonitrile), 132.4 (s, $H_3CS$–C=CH–*C*H), 136.7 (s, CH-benzonitrile), 137.0 (s, $C_2N_2$), 137.3 (s, CH-benzonitrile), 141.5 (s, *C*–$SCH_3$); $^{11}$B{$^1$H}-NMR ($C_6D_6$): $\delta$ = 27.5 (s); MS–EI (*m*/*z*): 421.1 [M$^+$].

### 2[3′-Cyano-4′(4″-cyanophenylethynyl)phenyl]-1,3-diethyl-1,3,2-benzodiazaborole (8)

Analogously a chilled solution (−110 °C, 40 mL) of 5-bromo-2-[(4-cyanophenyl)ethynyl]benzonitrile (0.88 g, 2.87 mmol) was treated with a 1.6 M *n*-butyllithium solution in *n*-hexane (1.8 mL, 2.88 mmol) before an equimolar amount of **1** (0.70 g, 2.77 mmol) in 5 mL was added. Solvent was removed as described and the residue extracted with *n*-hexane for 3 d, to yield a microcrystalline light green precipitate. This solid was separated and recrystallized from THF to afford 0.89 g (77% yield) of colorless crystalline **8**.

Found C 77.90, H 5.27, N 13.71%; $C_{26}H_{21}BN_4$ requires C 78.01, H 5.29, N, 14.00%; $^1$H-NMR ($CDCl_3$): $\delta$ = 1.32 (t, $J_{HH}$ = 7.2 Hz, 6H, $CH_2CH_3$), 3.76 (q, $J_{HH}$ = 7.2 Hz, 4H, $CH_2CH_3$), 7.09 (m, 2H, C*H*=CH–CH=C*H*), 7.15 (m, 2H, CH=C*H*–C*H*=CH), 7.66 (d, $J_{HH}$ = 8.2 Hz, 2H, CN–C=CH–C*H*), 7.71 (d, $J_{HH}$ = 8.2 Hz, 2H, CN–C=C*H*–CH), 7.73 (d, $J_{HH}$ = 7.9 Hz, 1H, H-benzonitrile), 7.79 (dd, $J_{HH}$ = 7.9, 1.2 Hz, 1H, H-benzonitrile), 7.89 (d, $J_{HH}$ = 1.2 Hz, H-benzonitrile); $^{13}$C{$^1$H}-NMR ($CDCl_3$) $\delta$ = 16.4 (s, $CH_2CH_3$), 37.8 (s, $CH_2CH_3$), 89.7, 94.3 (2 s, C≡C), 109.4 (s, *C*H=CH–CH=*C*H), 112.6 (s, CN–*C*=CH–CH), 115.5 (s, *C*–CN), 117.7 (s, *C*N–C=CH–CH), 118.4 (s, C–*C*N), 119.4 (s, CH=*C*H–*C*H=CH), 126.0 (s, C–Ph), 126.9 (s, C-benzonitrile), 131.7 (s, CH-benzonitrile), 132.2 (s, CN–C=*C*H), 132.5 (s, CN–C=CH–*C*H), 136.8 (s, $C_2N_2$), 137.3 (s, CH-benzonitrile), 137.4 (s, CH-benzonitrile); $^{11}$B{$^1$H}-NMR ($CDCl_3$): $\delta$ = 27.4 (s); MS–EI (*m*/*z*): 400.2 [M$^+$].

**X-ray Crystallography.** Crystallographic data were collected with a Bruker Nonius Kappa CCD diffractometer with Mo-K$\alpha$ (graphite monochromator, $\lambda$ = 0.71073 Å) at 100 K. Crystallographic programmes used for structure solution and refinement were from SHELX-97.[19] The structures were solved by direct methods and were refined by using full-matrix least squares on $F^2$ of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions with $U$(H) = 1.2 $U_{eq}$ for $CH_2$ groups and $U$(H) = 1.5 $U_{eq}$

for $CH_3$ groups, except compound **7**, where hydrogens were refined isotropically. Supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.†

## Computational methods

All calculations were performed using the Gaussian 09[20] program package with the 6-311G(d,p) basis set (6-311+G(d,p) for polarisability). DFT has been shown to predict various molecular properties successfully.[21] All geometry optimizations were carried out with the B3LYP[22] functional and were followed by frequency calculations in order to verify that the stationary points obtained were true energy minima. Ionization energies (IE) were calculated using the CAM-B3LYP[22d] functional (which is particularly well suited for the Ionization Energies evaluation—see for example ref. 14*c*) with ΔSCF/TD–DFT, which means that separate SCF calculations were performed to optimize the orbitals of the ground state and the appropriate ionic state ($IE = E_{cation} - E_{neutral}$). The advantages of the most frequently employed ΔSCF/TD–DFT method of calculations of the first ionization energies have been demonstrated previously.[23] The TD–DFT[24] approach provides a first principal method for the calculation of excitation energies within a density functional context taking into account the low-lying ion calculated by the ΔSCF method.

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